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3,446,738

ESTER BASE LUBRICANT COMPOSITIONS CONTAINING AN AROMATIC AMINE AND AN ORGANIC THIOPHOSPHITE OR THIOPHOSPHONATE

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Int. Cl. C10m *1/24*
U.S. Cl. 252—46.7 12 Claims

ABSTRACT OF THE DISCLOSURE

Ester base lubricating compositions of high temperature oxidative resistance are provided containing small amounts of each of an ester base fluid soluble aromatic amine, such as N-phenyl-alpha-naphthylamine, and an ester base fluid soluble organic thiophosphite or thiophosphonate, such as trilauryltrithiophosphite or dicresylphenylthiophosphonate. While these phosphorous compounds are not by themselves effective high temperature antioxidants in ester base lubricating oils, their combination with the aromatic amines affords oxidative resistance to ester base lubricating oils at high temperatures in excess of 400° F.

This invention relates to ester-based lubricant compositions containing a novel combination of additive agents. More particularly the present invention relates to ester-based lubricant compositions which exhibit increased oxidation resistance.

Organic compounds, such as lubricating oils, undergo oxidation upon exposure to air. This process is accentuated by elevated temperatures such as occur in engines and other operating machinery. When such organic compositions are used as motor or machnery lubricants, their stability is still further drastically reduced due to their contact with metal surfaces which give up metallic particles into the lubricant. Such abraded or dissolved metals or metal salts appear to act as oxidation catalysts in the lubricant causing the formation of primary oxidation products which in turn cause further degradation of the organic compounds present in the composition. Problems of this nature are encountered in mineral oils but appear to be particularly limiting in synthetic oleaginous fluids exemplified by esters.

The development of modern high speed jet turbine aircraft engines necessitates the search for lubricants which are resistant to high temperature oxidative degradation. Jet turbines are actuated by the energy of a burning fuel and are used to drive compressors which provide large amounts of air for the burning of the fuel. The combustion of the fuel provides the energy for driving the compressors with the remainder of the useful energy going into the propulsion of the aircraft. Jet turbine bearings are lubricated by pumping a lubricant to the bearings from a reservoir in a closed system. The design of more powerful jet turbines has led to an increase in the lubricant reservoir temperature and to greater difficulty in maintaining lubricant stability under the more severe conditions. For example, a lubricant which will operate satisfactorily at a reservoir temperature of 250° F. may sludge badly, build up viscosity, develop high acidity and corrode metals at a reservoir temperature of 440° F.

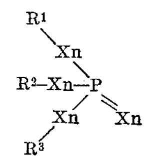
Thus jet turbine service requires a lubricant of superior thermal and oxidation stability as well as satisfactory physical characteristics in terms of viscosity, flash point, volatility, and load carrying properties. To arrive at such a lubricant it has been the general practice to add an antioxidant and other additives, such as foam inhibitors, anti-wear agents, etc., to a base fluid of suitable properties.

Numerous oxidation and corrosion inhibitors have been found for use in lubricating compositions and many combinations thereof also have been tested. For instance, anti-oxidants such as phenothiazine; phenyl-α-naphthylamine; 5-ethyl-10, 10-diphenylphenazasiline; etc. are well known in the art. The known inhibitors, however, are not adequate to provide the superior oxidation resistance now needed. Moreover, the effectiveness of these known inhibitors is greatly impaired in the presence of metal.

It is the object of this invention to provide an ester base synthetic lubricant having superior resistance toward oxidative and thermal degradation. It is a further object to protect and improve this resistance against the detrimental effects of metals with the use of suitable additives.

The present invention provides an improved ester-based lubricant composition containing small amounts effective to retard oxidation, of each of a defined sulfur and phosphorous-containing organic compound and an aromatic amine.

The sulfur phosphorous-containing organic compounds of our composition used in minor amounts are soluble in the base ester oil to the extent present and have the formula:



where

X is O or S, at least one being S
n=0 or 1, at least three n's being 1
R^1, R^2, R^3 are alkyl or aromatic groups

R^1, R^2 and R^3 are aromatic, including mixed aryl-alkyl, or alkyl, including cycloalkyl, hydrocarbon radicals of up to about 18 carbon atoms, and preferably of about 4 to 12 carbon atoms, whose adjacent carbon atoms are no closer than 1.40 A. (i.e. a non-olefinic, non-acetylenic). In any given compound the R radicals may be the same or differently selected from the group of radicals given above. Exemplary of the R aromatic radicals are phenyl and naphthyl groups, which groups may be substituted with non-deleterious substituents such as one or more lower alkyl radicals. The R alkyl radicals may be straight chain, branched, or cyclic alkyls which may be substituted with non-deleterious substituents, for example, ethyl, butyl, hexyl, octyl and iso-octyl.

Especially effective sulfur and phosphorous-containing compounds for use with the aromatic amines in our lubricant composition are dicresyl phenylthiophosphonate, trilauryl trithiophosphite, O,O,O-tributyl thiophosphate, phenylethylene thiophosphite, etc. Other thiophosphonates, thiophosphites, thiophosphates and other esters of phosphorous-containing acids which contain one or more sulfur atoms in the molecule can also be used. Examples of other suitable thiophosphonates include triphenyl thiophosphonate, tricresyl thiophosphonate, diethyl cresyl thiophosphonate, lauryl methyl benzene thiophosphonate, dicresyl lauryl thiophosphonate, dioctyl phenylthiophosphonate, dilauryl chloromethyl dithiophosphonate. Examples of other suitable thiophosphites include tributyl triothiophosphite, trioctyl trithiophosphite, tricresyl trithiophosphite, trilauryl dithiophosphite, trioctyl monothiophosphite, dioctyl monothiophosphite and S,S-dioctyl phenyl dithiophosphite. Examples of other suitable thiophosphates include dilauryl thiophosphate, lauryl ethyl thiophosphate, monophenyl thiophosphate, diphenyl thiophosphate, dicresyl octyl thiophosphate, dioctyl dithiophosphate, dioctylphenyl dithiophosphate, trilauryl trithiophosphate, and trilauryl tetrathiophosphate. Examples of other S- and P-containing compounds suitable for use as antioxidants with aromatic amines include trioctyl thiophosphinate, trioctyl dithiophosphinate, tricresyl thiophosphinate, S-lauryl diphenylthiophospinate, dilauryl amidothiophosphate, di-isoamyl amidothiophosphate and N-butyl dioctyl amidothiophosphate.

The aromatic amine component of the invention is soluble in the ester fluid to the extent present and can be represented by the following general formula:

$$\begin{array}{c} Q'\text{—}N\text{—}H \\ | \\ Q \end{array}$$

wherein Q is a monovalent hydrocarbon of 1 to 20 carbons, preferably 6 to 12 carbon atoms, whose adjacent carbon atoms are no closer than 1.40 A. (i.e. a non-olefinic, non-acetylenic, monovalent hydrocarbon), and Q′ is an aromatic hydrocarbon radical of 6 to 12 or 16 carbon atoms. Thus Q can be an alkyl group, including cycloalkyl, or an aromatic group. Preferably both Q and Q′ are aromatic, and often at least one is a fused ring aromatic, e.g. naphthyl. Q and Q′ can be substituted with non-interfering substituents such as alkyl groups and amine groups, preferably alkyl or aromatic amines, and Q and Q′ can be linked together by means of a non-interfering element such as carbon, sulfur and oxygen. Illustrative of suitable amines are phenothiazine, N-phenyl-α-naphthyl amine; di(α-naphthyl amine); N,N′-diphenyl para-phenylene diamine; N,N′-dioctyl para-phenylene diamine, N,N′-heptylphenyl para-phenylene diamine; diphenyl amine, n-butyl phenyl(α-naphthyl)amine, di-beta-naphthylamine, N-phenyl-decyl amine, N-phenyl-isooctyl amine, diphenyl amine, monomethylaniline, phenoxazine and carbazole.

The additives of the invention are incorporated in the base oil in amounts sufficient to retard oxidation of the oil, and the concentrations employed for optimum results may be dependent on the particular base oil and second additive component selected. Ordinarily about 0.05 to 5%, preferably about 0.1 to 2%, by weight of each of the phosphorous-sulfur compound and the amine additive component provide satisfactory results.

The lubricant composition of this invention includes as the major component a base oil which is an ester of lubricating viscosity which may be, for instance, a simple ester or compounds having multiple ester groupings such as complex esters, di- or other polyesters, and polymer esters. These esters are usually made from mono- and poly-functional aliphatic alcohols or alkanols, and aliphatic mono- and poly-carboxylic or alkanoic acids. Frequently, the alcohols and acids have about 4 to 12 carbon atoms. The reaction product of a mono-functional alcohol and a monocarboxylic acid is usually considered to be a simple ester. A diester is usually considered to be the reaction product of 1 mole of a dicarboxylic acid, say of 6 to 10 carbon atoms, with 2 moles of a monohydric alcohol or of 1 mole of a glycol, for instance of 4 to 10 carbon atoms, with two moles of a monocarboxylic acid, e.g. of 4 to 10 carbon atoms. The diesters frequently contain from 20 to 40 carbon atoms.

A complex ester is usually considered to be of the type X—Y—Z—Y—X in which X represents a monoalcohol residue. Y represents a dicarboxylic acid residue and Z represents a glycol residue and the linkages are ester linkages. Those esters, wherein X represents a monoacid residue, Y represents a glycol residue and Z represents a dibasic acid residue are also considered to be complex esters. The complex esters often have 30 to 50 carbon atoms.

Polymer esters or "polyester bright stocks" can be prepared by direct esterification of dicarboxylic acids with glycols in about equimolar quantities. The polyesterification reaction is usually continued until the product has a kinematic viscosity from about 15 to 200 centistokes at 210° F., and preferably 40 to 130 centistokes at 210° F.

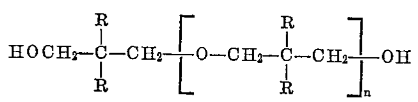
Although each of these products in itself is useful as a lubricant, they are particularly useful when added or blended with each other in synthetic lubricant compositions. These esters and blends have been found to be especially adaptable to the conditions to which turbine engines are exposed, since they can be formulated to give a desirable combination of high flash point, low pour point, and high viscosity at elevated temperatures, and need contain no additives which might leave a residue upon volatilization. In addition, many complex esters have shown good stability to shear. Natural esters, such as castor oil may be employed and also be included in the blends, as may be small amounts of a foam inhibitor such as a methyl silicone polymer or other additives or lubricant components to provide a particular characteristic, for instance, extreme pressure or load carrying agents, corrosion inhibitors, etc., can be added.

The monohydric alcohols employed in these esters usually contain about 4 to 20 carbon atoms and are generally aliphatic. Preferably the alcohol contains up to about 12 carbon atoms. Useful alkanols include butyl, hexyl, methyl, iso-octyl and dodecyl alcohols, C_{12} oxo alcohols and octadecyl alcohols. C_8 to C_{10} branched chain primary alcohols are frequently used to improve the low temperature viscosity of the finished lubricant composition. Alcohols such as n-decanol, 2-ethyl-hexanol "oxo" alcohols, prepared by the reaction of carbon monoxide and hydrogen upon the olefins obtainable from petroleum products such as di-isobutylene and C_7 olefins, other alcohols such as butyl carbitol, tripropylene glycol mono-isopropyl ether, dipropylene glycol mono-isopropyl ether, and products such as "Tergitol 3A3" which has the formula $C_{13}H_{27}O(CH_2CH_2O)_3H$, are suitable alcohols for use to produce the desired lubricant. If the alcohol has no hydrogens on the beta carbon atoms, it is neo-structured; and esters of such alcohols are often preferred. In particular, the neo-C_8 alcohol—2,2,4-trimethyl-pentanol-1—gives lubricating diesters or complex esters suitable for blending with diesters to produce lubricants which meet stringent viscosity requirements. Iso-octanol and iso-decanol are alcohol mixtures made by the oxo process from C_3–C_4 copolymer heptenes. The cut which makes up iso-octanol usually contains about 17% 3,4-dimethylhexanol; 29% 3,5-dimethylhexanol; 25% 4,5-dimethylhexanol; 1.4% 5,5-dimethylhexanol; 16% of a mixture of 3-methylheptanol and 5-ethylheptanol; 2.3% 4-ethylhexanol; 4.3% α-alkyl alkanols and 5% other materials.

Generally, the glycols contain from about 4 to 12 carbon atoms; however, if desired they could contain a greater number. Among the specific glycols which can be employed are 2-ethyl-1,3-hexanediol, 2-propyl-3,3-heptanediol, 2-methyl-1,3-pentanediol, 2-butyl-1,3-butanediol, 2,4-diphenyl-1,3-butanediol, and 2,4-dimesityl-1,3-butanediol. In addition to these glycols, ether glycols may be used, for instance, where the alkylene radical contains 2 to 4 carbon atoms such as diethylene glycol, dipropylene glycol and other glycols up to 1000 to 2000 molecular weight. The most popular glycols for the manufacture of ester lubricants appear to be polypropylene glycols having a molecular weight of about 100–300 and 2-ethylhexanediol. The 2,2-dimethyl glycols, such as neopentyl glycol have been shown to impart heat stability to the final blends. Minor amounts of ether glycols or other materials can be present as long as the desired properties of the product are not unduly deleteriously affected.

One group of useful monocarboxylic acids includes those of 8 to 18 or even 24 carbon atoms such as stearic, lauric, etc. The carboxylic acids employed in making ester lubricants will often contain from about 4 to 12 carbon atoms. Suitable acids are described in U.S. Patent No. 2,575,195, and include the aliphatic dibasic acids of branched or straight chain structures which are saturated or unsaturated. The preferred acids are the saturated aliphatic carboxylic acids containing not more than about 12 carbon atoms, and mixtures of these acids. Such acids include succinic, adipic, suberic, azelaic, and sebacic acids and "isosebacic" acid which is a mixture of α-ethyl suberic acid, α,α'-diethyl adipic acid and sebacic acid. This composite of acids is attractive from the viewpoint of economy and availability since it is made from petroleum hydrocarbons rather than the natural oils and fats which are used in the manufacture of many other dicarboxylic acids, which natural oils and fats are frequently in short supply. The preferred dibasic acids are sebacic and azelaic or mixtures thereof. Minor amounts of adipic used with a major amount of sebacic may also be used with advantage.

The ester base oils to which incorporation of the additive combination of the invention is particularly advantageous are the oils commonly referred to as neopentyl polyol polyesters, having more than one ester group. These are the esters of aliphatic carboxylic acids, generally alkanoic acids, of about 4 to 12 carbon atoms, and a polyhydric alkanol free of beta hydrogen, i.e. containing no hydrogen on the beta carbon atoms, and including the di(polyhydric alcohol) ethers. The polyhydric alcohol generally contains about 2 to 6 hydroxy groups and about 5 to 20, preferably 5 to 12 carbon atoms. Illustrative of the alcohols are those having the general formula:

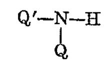


wherein n is 0 to 1 and R is a lower alkyl group, preferably of about 1 to 4 carbon atoms, which can be straight or branched chain, or a hydroxy methyl group. These esters can be made by reacting a mole of the alcohol with about 2 moles up to the stoichiometric equivalent of the carboxylic acid.

Illustrative of polyhydric alcohols free of beta hydrogen are neopentyl glycol, trimethylolethane, trimethylolpropane, pentaerythritol, dipentaerythritol, 2-butyl-2-ethyl-1,3-propanediol, etc. Suitable aliphatic carboxylic acids with which the polyhydric alcohols free of beta hydrogen may be esterified are n-butyric acid, isobutyric acid, n-pentanoic acid, isopentanoic acid, n-heptanoic acid, isoheptanoic acid, n-isoheptanoic acid, n-octanoic acid, isooctanoic acid, pelargonic acid, n-decanoic acid, lauric acid, myristic acid, stearic acid, n-dodecanoic acid, valeric acid, n-hexabutyric acid, etc.

The effectiveness of the combination of additives of the present invention as an antioxidant in synthetic ester lubricants is apparent from the tests reported below. The times to the end of the inhibition period and to the end of the test are designated T*i* and T*t*, respectively, and the volume of oxygen absorbed is designated V*t*. It can be seen that the phosphorus and sulfur-containing additives of the invention are not, by themselves, effective antioxidants. However, their combinations with the aromatic amines are quite effective.

where X is selected from the group consisting of sulfur and oxygen, at least one X being sulfur, n is 0 or 1 with three n's being 1 and one n being 0, R^1, R^2 and R^3 are selected from the group consisting of alkyl and aromatic hydrocarbon radicals of up to about 18 carbon atoms and an ester base fluid soluble aromatic amine having the general formula

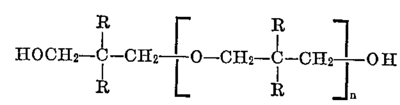


where Q is a non-olefinic, non-acetylenic monovalent hydrocarbon radical of 1 to 20 carbon atoms and Q' is an aromatic hydrocarbon radical of 6 to 16 carbon atoms, said amounts being effective to retard oxidation of said ester base fluid at temperatures in excess of 400° F., said ester base fluid being an ester of alkanol of 4 to 20 carbon atoms and alkane carboxylic acid of 4 to 18 carbon atoms.

2. The lubricant composition of claim **1**, wherein Q is an aromatic hydrocarbon radical and Q and Q' each have 6 to 12 carbon atoms.

3. The lubricant of claim **2** wherein the sulfur and phosphorous-containing compound is present in an amount of about .01 to 2% by weight and the aromatic amine is present in an amount of about 0.1 to 2% by weight.

4. The lubricant composition of claim **1** wherein the ester base fluid is an ester of an alkanol having the general formula:



wherein n is 0 to 1 and R is selected from the group consisting of lower alkyl radicals and hydroxy methyl.

5. The lubricant composition of claim **4** wherein the aromatic amine is N-phenyl-α-naphthylamine.

6. The lubricant composition of claim **5** wherein the sulfur and phosphorous-containing compound and aromatic amine are each present in the amount of about 0.01 to 2%.

7. The lubricant composition of claim 6 wherein the sulfur and phosphorous-containing compound is dicresyl phenyl thiophosphonate.

8. The lubricant composition of claim **6** wherein the sulfur and phosphorous-containing compound is trilauryltrithiophosphite.

9. The lubricant composition of claim **1** wherein at least one of R^1, R^2 or R^3 is an aromatic hydrocarbon radical of up to 18 carbon atoms.

10. A lubricant composition consisting essentially of a major amount of an ester base fluid of lubricating viscosity

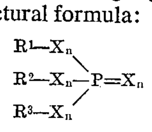
TABLE I

Test No.[1]	Base Fluid	Aromatic Amine	Weight Percent	Sulfur-Phosphorous Additive	Weight Percent	O₂ Absorption Test Data: Ti (min.)	Tt (min.)	Vt (ml.)
1	B[2]	None		None		10	99	2,500
2	B	do		Dicresylphenylthiphosphonate	1.0	10	96	2,500
3	B	N-phenyl-α-naphthylamine	0.5	None		70	103	2,500
4	B	do	0.5	Dicresylphenylthiophosphonate	1.0	243	338	2,500
5	B	do	0.5	Trilauryltrithiophosphite	1.0	>257	257	2,500
6	B	do	0.5	O,O,O-tributylthiophosphate	1.0	143	195	2,500
7	B	do	0.5	Phenylethylenethiophosphate	1.0	197	284	2,500

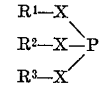
[1] Test conditions=450° F., 1 cu. ft. O_2/hr., 75 g. sample.
[2] 20% diisooctyl azelate and 80% complex ester of neopentyl glycol, azelaic acid and isooctyl alcohol (mole ratio 1:2:2).

It is claimed:

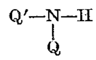
1. A lubricant composition consisting essentially of a major amount of an ester base fluid of lubricating viscosity and small amounts of each of an ester base fluid soluble sulfur and phosphorous-containing organic compound having the following structural formula:



and small amounts of each of an ester base fluid soluble thiophosphite having the following structural formula:

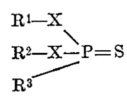


where X is selected from the group consisting of sulfur and oxygen, at least one X being sulfur, R^1, R^2 and R^3 are selected from the group consisting of alkyl and aromatic hydrocarbon radicals of up to about 18 carbon atoms and an ester base fluid soluble aromatic amine having the general formula:

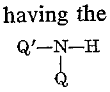


wherein Q is a non-olefinic, non-acetylenic monovalent hydrocarbon radical of 1 to 20 carbon atoms and Q′ is an aromatic hydrocarbon radical of 6 to 16 carbon atoms, said amounts being effective to retard oxidation of said ester base fluid at temperatures in excess of 400° F., said ester base fluid being an ester of alkanol of 4 to 20 carbon atoms and alkane carboxylic acid of 4 to 18 carbon atoms.

11. A lubricant composition consisting essentially of a major amount of an ester base fluid of lubricating viscosity and small amounts of each of an ester base fluid soluble thiophosphonate having the following structural formula:

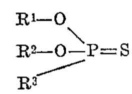


wherein X is selected from the group consisting of sulfur and oxygen, R^1, R^2 and R^3 are selected from the group consisting of alkyl and aromatic hydrocarbon radicals of up to about 18 carbon atoms and an ester base fluid soluble aromatic amine having the general formula:

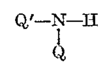


wherein Q is a non-olefinic, non-acetylenic monovalent hydrocarbon radical of 1 to 20 carbon atoms and Q′ is an aromatic hydrocarbon radical of 6 to 16 carbon atoms, said amounts being effective to retard oxidation of said ester base fluid at temperatures in excess of 400° F., said ester base fluid being an ester of alkanol of 4 to 20 carbon atoms and alkane carboxylic acid of 4 to 18 carbon atoms.

12. A lubricant composition consisting essentially of a major amount of an ester base fluid of lubricating viscosity and small amounts of each of an ester base fluid soluble thiophosphonate having the following structural formula:



R^1, R^2 and R^3 are selected from the group consisting of alkyl and aromatic hydrocarbon radicals of up to about 18 carbon atoms and an ester base fluid soluble aromatic amine having the general formula:



where Q is a non-olefinic, non-acetylenic monovalent hydrocarbon radical of 1 to 20 carbon atoms and Q′ is an aromatic hydrocarbon radical of 6 to 16 carbon atoms, said amounts being effective to retard oxidation of said ester base fluid at temperatures in excess of 400° F., said ester base fluid being an ester of alkanol of 4 to 20 carbon atoms and alkane carboxylic acid of 4 to 18 carbon atoms.

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US. Cl. XR.

252—46.6

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,446,738 Dated May 27, 1969

Inventor(s) Tai S. Chao and Daniel B. Eickemeyer

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 8, in the References Cited

"3,282,905" should read --2,382,905--.

SIG D A
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JAN 6 - 1970

(SEAL)
Attest:

Edward M. Fletcher, Jr.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents